ORIGINAL ARTICLE

Adsorption behavior of some metal ions on hydrated amorphous titanium dioxide surface

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Abstract

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Adsorption behavior of some metal ions on hydrated amorphous titanium dioxide surface
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Titanium dioxide was prepared from titanium tetrachloride and diluted ammonia solution at low temperature. The product obtained was characterized by XRD, EDXRF, TGA, DSC, and FT-IR techniques. It was found that the product was in the form of hydrated amorphous titanium dioxide, $TiO_2 \cdot 1.6H_2O$ (ha-TiO_2). Ha-TiO_2 exhibits high BET surface area at 449 m^2/g. Adsorptions of metal ions onto the ha-TiO_2 surface were investigated in the batch equilibrium experiments, using Mn(II), Fe(III), Cu(II), and Pb(II) solutions. The concentrations of metal ions were determined by atomic absorption spectrometer. The adsorption isotherms of all metal ions were studied at pH 7. The adsorption of Mn(II), Cu(II), and Pb(II) ions on ha-TiO_2 conformed to the Langmuir isotherm while that of Fe(III) fit equally well to both Langmuir and Freundlich isotherms.

Key words : titanium dioxide, amorphous titanium dioxide, metal oxide surface, Degussa P25, metal ion adsorption, Langmuir isotherm, Freundlich isotherm, solid-phase extraction, preconcentration

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พฤติกรรมการดูดซับโลหะไอออนบางชนิดบนพื้นผิวไทเทเนียมไดออกไซด์อสัณฐานชนิดไฮเดรต

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ได้สังเคราะห์ไทเทเนียมไดออกไซด์จากปฏิกิริยาระหว่างไทเทเนียมเตตระคลอไรด์กับสารละลายแอมโมเนียเจือจางที่อุณหภูมิต่ำ ผลิตภัณฑ์ที่ได้นำไปศึกษาด้วยเทคนิค XRD, EDXRF, TGA, DSC และ FT-IR ซึ่งพบว่าเป็นไทเทเนียมไดออกไซด์อสัณฐานชนิดไฮเดรตมีสูตรเป็น $TiO_2.1.6H_2O$ (ซึ่งจะแทนด้วยสัญลักษณ์ ha-TiO_2) นำสาร ha-TiO_2 นี้ไปวัดพื้นที่ผิวโดยวิธี BET พบว่ามีพื้นที่ผิว 449 m^2/g ซึ่งค่อนข้างสูง ได้ศึกษาการดูดซับไอออนโลหะบนพื้นผิวของ ha-TiO_2 นี้โดยใช้สารละลายที่มีไอออน Mn(II), Fe(III), Cu(II) และ Pb(II) ตรวจวัดความเข้มข้นของสารละลายโลหะไอออนโดยเครื่องอะตอมมิกแอบซอร์พชัน ศึกษาการดูดซับของโลหะไอออนที่สภาวะความเป็นกรด-เบสของสารละลายเท่ากับ pH 7 ข้อมูลการดูดซับเมื่อนำมาสร้างกราฟพบว่าไอออน Mn(II), Cu(II) และ Pb(II) มีพฤติกรรมสอดคล้องกับไอโซเทิร์มแลงเมียร์ ส่วนไอออน Fe(III) อาจเป็นได้ทั้งไอโซเทิร์มแลงเมียร์และไอโซเทิร์มฟรอยด์ลิค

Titanium dioxide (TiO_2), encompassing all its three crystal forms, has wide applications in various fields. One of the most recent applications is as a photocatalyst (Sclafani *et al.*, 1990; Matthews, 1991; Hua *et al.*, 1995; Robertson *et al.*, 1997; Wang and Adesina, 1997; Kosanic′,1998; Tatsuma *et al.*,1999). Another promising aspect is as an inorganic ion exchanger and sorbent due to its high chemical stability and high ion exchange capacity, which may find application in solid-phase extraction (SPE) (Vassileva *et al.*, 1996). The study centered around the latter aspect usually involving adsorption of metal cations on the titanium dioxide surface. TiO_2's used in these studies were in the form of anatase or a mixture of anatase and rutile (Degussa P25) (Malati and Smith, 1979; Malati *et al.,* 1982; Ottaviani *et al.*, 1985; Vohra and Davis, 1997; Esumi *et al.,* 1998; Poznyak *et al.*, 1999). The use of amorphous TiO_2 in this regard could only scarcely be found (Abe *et al.*, 1989).

In this work we would like to report the results from our studies with hydrated amorphous TiO_2 (ha-TiO_2) with four metal ions: Mn(II), Fe(III), Cu(II), Pb(II) . While we were studying ha-TiO_2 on its photocatalyst activity (Randorn *et al.*, 2004), we observed that ha-TiO_2 possesses a rather high specific surface area which might be useful if it is to be used as a sorbent for metal ions. The specific surface area of ha-TiO_2 is higher than that found with commercial anatase and Degussa P25.

Materials and Methods

Synthesis of ha-TiO_2

Ha-TiO_2 used in this work was prepared from titanium tetrachloride and diluted ammonia solution. NH_3 solution (2.93 M, ca. 240 mL, AR, J.T.Baker) was added slowly to $TiCl_4$ (30 mL, 0.267 mol, AR, Carlo Erba) in a 2-necked round bottom flask which was placed in an ice-water bath and stirred simultaneously until the white precipitate was obtained. The precipitate was filtered gravimetrically and subsequently washed with distilled water until free of chloride and ammonium ions ($AgNO_3$ and NaOH tests, respectively). The product obtained, ha-TiO_2, was dried at 105ºC, ground and sieved to -200 mesh size (75 µm) when used.

Adsorption isotherm experiments

The adsorption isotherms between ha-TiO_2 and metal ions (Mn(II), Fe(III), Cu(II), and Pb(II))

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were investigated. In each case, using standard solutions (1000 mg/L, Merck), various concentrations of sample solutions were prepared (5, 15, 20, 25, 50, 75, 100, 150, and 200 mg/L for Mn(II); 2, 4, 5, 10, 12, 15, and 25 mg/L for Fe(III); 25, 35, 50,75, 100,150, 200, 250, and 300 mg/L for Cu(II); 5, 10, 15, 20, 25, 50, 75, 100 , 200, 300, and 400 mg/L for Pb(II)). The solutions were adjusted to pH 7 with HNO_3 and NH_3 solutions. A portion of each metal ion solution (30 mL for Mn(II), 50 mL for Fe(III), 25 mL for Cu(II), and 50 mL for Pb(II)) was pipetted into a beaker containing pre-weighed ha-TiO_2 (0.05 g for Mn(II), Fe(III), Cu(II), and 0.025 g for Pb(II)) and stirred at room temperature (10 mins for Cu(II), Mn(II); 15 mins for Fe(III), Pb(II)). After reaching equilibrium, the solution was separated by centrifugation and the concentration of metal ion in the liquid phase (Ce, mg/L) was determined by AAS (Aanalyst 300, Perkin Elmer, U.S.A.).

Adsorption capacity measurements

The comparison of the adsorption capacities between ha-TiO_2 and the commercial TiO_2 (anatase (Carlo Erba), Degussa P25, and rutile (TOA Co., Thailand)) was investigated by using single solution at pH 7 [75 mg/L for Mn(II), 15 mg/L for Fe(III), 200 mg/L for Cu(II), and 400 mg/L for Pb(II)]. After equilibrium, the aqueous phase was separated from TiO_2 by centrifugation and the residual concentration of metal ion (Ce, mg/L) was determined by AAS.

The amount of metal ion adsorbed per unit mass of TiO_2 (i.e., adsorption capacity, mg/g) was calculated by (Arpa *et al.*, 2000)

$$Q_e = \frac{[(C_0 - C_e) \times V]}{[m \times 1000]}$$

where C_0 and C_e are the initial and the residual equilibrium concentrations of metal ion in aqueous phase (mg/L), respectively, V is the volume of the aqueous phase (mL) and m is the mass of TiO_2 used (g).

Results and Discussion

Physical properties of ha-TiO_2

Ha-TiO_2 prepared by this method existed only as an amorphous form as evidenced by its XRD (Philips PW 3710) pattern (Figure 1) and the purity of ha-TiO_2 was checked by EDXRF (Spectrace 5000, Spectrace Instruments, Inc., Mountainview, California) from which only the Ti K lines could be seen in the spectrum (Figure 2) indicating no contamination by other species or heavy elements. The present of H_2O and NH_4^+ (*vide infra*) could not be detected by EDXRF due to too low characteristic energies of oxygen and nitrogen atoms.

The FT-IR (EQUINOX 55, Bruker, Germany) spectrum of ha-TiO_2 (Figure 3) showed a large broad band at 3100-3500 cm^{-1} and rather narrow

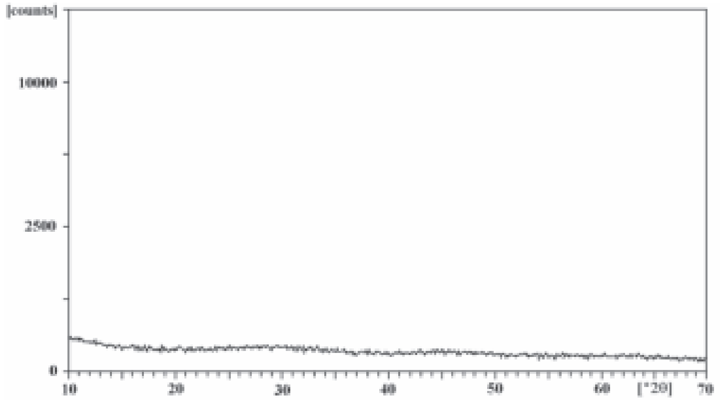

Figure 1. XRD pattern of ha-TiO_2.

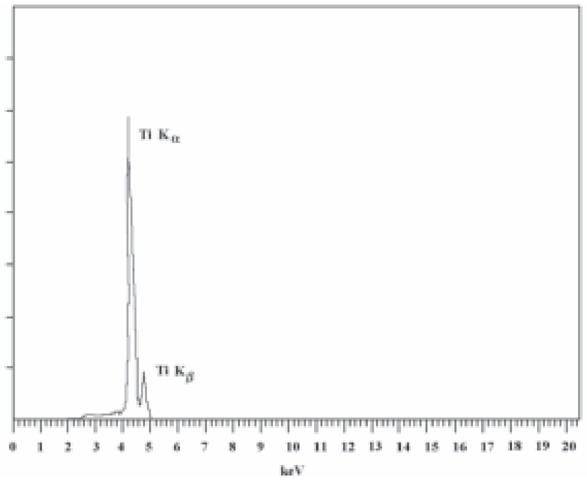

Figure 2. EDXRF spectrum of ha-TiO$_2$.

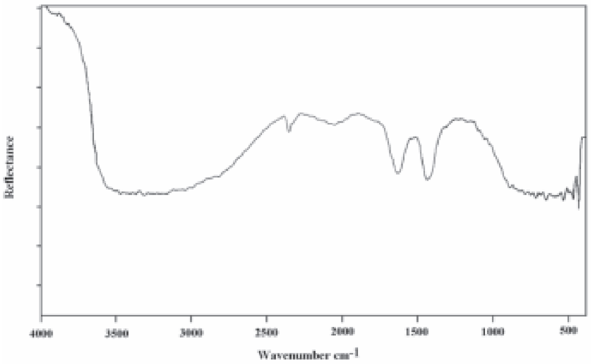

Figure 3. FT-IR spectrum (reflectance mode) of ha-TiO$_2$.

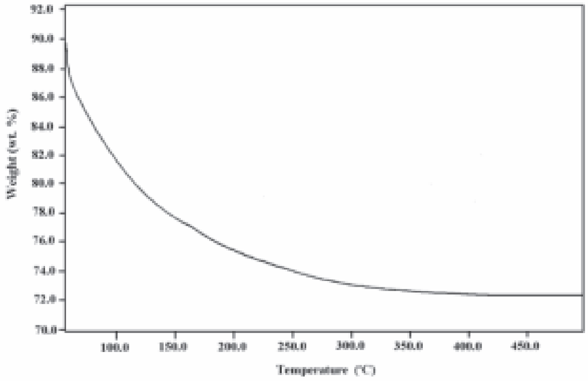

Figure 4. TGA curve of ha-TiO$_2$.

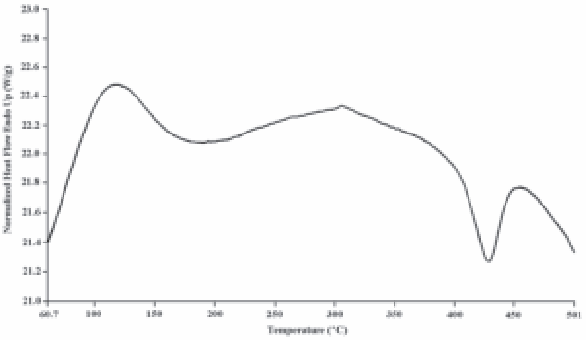

Figure 5. DSC spectrum of ha-TiO$_2$.

bands at 1638 and 1432 cm^{-1}, together with one weak absorption at 442 cm^{-1}. The broad one at 3100-3500 cm^{-1} can be assigned to both of ν_{O-H} and ν_{N-H} (stretching mode) while those at 1638 and 1432 cm^{-1} can be assigned to the δ_{O-H} and δ_{N-H} (bending mode) of hydroxyl (OH) and ammonium

(NH_4^+) groups, respectively (Khalil and Zaki, 1997; Youn *et al.*, 1999). The absorption at 442 cm^{-1} can be assigned to the ν_{Ti-O} (stretching mode) of Ti-O bond (Zhang *et al.*, 2002). Therefore, the FT-IR spectra confirmed the presence of impurities such as NH_4^+ and H_2O at the surface of ha-TiO_2. The amount of NH_4^+ was, however, very small ca. 1.3-1.8% by elemental analysis for nitrogen content. This small amount of nitrogen also rendered it undetectable by SEM/EDX and WDXRF.

The TGA (TGA7, Perkin Elmer, U.S.A.) curve of ha-TiO_2 (Figure 4) shows a gradual weight loss commencing near 50ºC and coming to completion near 450ºC. The initial weight loss in the range 50-150ºC occurs at higher rate than that taking place at higher temperatures. The total weight loss of the product was about 25.98% equivalent to the decomposition of the product $TiO_2 \cdot 1.6H_2O$ into TiO_2. A similar result was reported for the hydrolysis product of $Ti(OPri)_4$ where the total weight loss was found to be 31% due to the decomposition of $TiO_2 \cdot 2H_2O$ into TiO_2 (Khalil and Zaki, 1997).

The DSC (DSC7, Perkin Elmer., U.S.A.) pattern of TiO_2 sample (Figure 5) showed an endothermic peak at *ca.* 109ºC which could be attributted to liberation or decomposition of water molecules. A characteristic exothermic peak was also observed at *ca.* 426ºC and was attributable to crystallization of amorphous phase to anatase. A similar result was reported for the crystallization temperatures by Youn *et al.*, (Youn *et al.*, 1999). They suggested that DSC and XRD results revealed crystallization temperatures (anatase) of 390 and 467ºC for non-rinsed (water-washed only) and ethanol/butanol-rinsed powders, respectively. Ha, *et al.*, reported the crystallization temperatures for the titanium dioxide powders at 440ºC (Ha *et al.*, 2000).

The results from XRD, FT-IR, TGA, DSC led to the conclusion that ha-TiO_2 was a hydrated amorphous titanium dioxide with some of NH_4^+ as impurity. The weight loss from TGA hinted that it can be formulated, approximately, as $TiO_2 \cdot 1.6 H_2O$. The NH_4^+ ion that present most likely came from the NH_3 that was used in large amount during the hydrolysis stage and was not washed out completely at the washing stage.

The presence of H_2O (and minute amount of NH_4^+) in ha-TiO_2 may have some effect on the specific surface area which was measured by BET method (Autosorb-1-C, Quantachrome). The surface area of ha-TiO_2 at 449 m^2/g was rather high for titanium dioxide of any forms. In order to corroborate this high value, other samples of TiO_2, such as the commercially available anatase from Carlo Erba, rutile from a paint factory (TOA, Thailand), and Degussa P25, were also subjected to the same measurement under the same conditions. The results of these surface area measurements were: anatase 10.72, rutile 16.08, and Degussa P25 54.50 m^2/g. These values are comparable to those reported earlier: anatase 5.9-17.30, rutile 20, and Degussa P25 50-55 m^2/g (Sclafani *et al.*, 1990; Tanaka *et al.*, 1991; Matthews, 1991; Hoffman *et al.*, 1995; Wang and Adesina, 1997; Hous *et al.*, 2001).

Nature of metal ion adsorptions by ha-TiO_2

The adsorption of metal ions on ha-TiO_2 reached equilibrium in 10 minutes for Mn (II) and Cu(II) and 15 minutes for Fe(III) and Pb(II). In general, the adsorption of cations by hydrous metal oxides is frequently found to be extremely rapid, most of the exchange occuring within a matter of minutes (Kinniburg and Jackson, 1981). Vassileva *et al.* (1996) found that it took about 5 minutes to reach equilibrium for the adsorption of metal ions on TiO_2 (anatase) under static conditions. For ha-TiO_2, at lower concentrations, adsorptions increase with increasing concentrations up to maximum concentrations which were 4, 8, 5, and 25 mg/L for Mn(II), Fe(III), Cu(II), and Pb(II), respectively. Sorptions for these four metal ions took place quantitatively in the following pH ranges: 3-7 for Mn(II), 5-9 for Fe(III), and 3-9 for both Cu(II) and Pb(II). Hence , the experimental condition was set up at pH 7 for the adsorption isotherm measurements.

Adsorption isotherm plots

Adsorption characteristics between the

adsorbent and adsorbate can be described by adsorption isotherms. In this work, the Langmuir and Freundlich isotherm plots were used for studying the adsorption data. These isotherms relate metal per unit weight of adsorbent (Qe, mg/g) to the residual equilibrium concentration of metal ions (Ce, mg/L). The Langmuir is usually used to analyse data by studying the relation between $1/Q_e$ and $1/C_e$. Whereas, the Freundlich is usually used to analyse data by studying the relation between log Q_e and log C_e. Figures 6-7 are the Langmuir and Freundlich isotherm plots , respectively, for Mn(II), Fe(III), Cu(II), and Pb(II).

To compare the reliability of these adsorption isotherms, the correlation coefficient (R^2) for each adsorption isotherm was calculated and shown in Table 1.Based on the values of the correlation coefficient (R^2) for the different isotherm plots, the Langmuir isotherm gives the best fit for the adsorption of Mn(II), Cu(II), and Pb(II) whereas the adsorption of Fe(III) seems to fit both Langmuir and Freundlich isotherms. The correlation coefficient (R^2) is a good criterion and means that the difference between experimental data and theoretical values is small when the value of the coefficient approaches 1 (Kim and Chung, 2001).

Comparison of the adsorption capacity

The adsorption capacity is an important factor, because it determines how much of metal ions from solution can be adsorbed by a certain amount of TiO_2. The results are presented in Table 2. It can be seen that the capacity of ha-TiO_2 is considerably higher than that of other TiO_2's, presumably because of the higher surface area of ha-TiO_2 (449 m^2/g). The adsorption capacity of the four comparative TiO_2's, i.e., anatase(syn), anatase (Carlo Erba), Degussa P25, and rutile(TOA), for Mn(II) were extremely low, practically nil, as

Table 1. The correlation coefficient (R^2) for adsorption isotherms of metal ions on ha-TiO_2.

	Mn(II)	Fe(III)	Cu(II)	Pb(II)
Langmuir isotherm	0.999	0.9775	0.9659	0.9828
Freundlich isotherm	0.8234	0.9768	0.8556	0.8956

Table 2. Comparison of adsorption capacity (mg/g) of TiO_2.

Samples	Adsorption capacity (mg/g)				Refs.
	Mn(II)	Fe(III)	Cu(II)	Pb(II)	
ha-TiO_2	24.92	14.85	84.79	618.79	this work
Anatase (syn)[a]	ca. 0	14.90	67.40	308.98	this work
Anatase (Carlo Erba)	ca. 0	14.90	71.15	194.28	this work
Degussa P25	ca. 0	14.90	63.63	219.41	this work
Rutile (TOA)	ca. 0	15.02	68.84	187.99	this work
T1(anatase, syn)	6.830	-	9.010	5.030	(Vassileva *et al*., 1996)[b]
T2(anatase, Fluka)	-	-	0.270	0.220	(Vassileva *et al*., 1996)[b]
Nanometer TiO_2	2.14	-	6.86	-	(Liang *et al*., 2001)[c]

a: This sample of anatase was prepared by the same method as that reported in Vassileva *et al.*, 1996. Surface area of this prepared sample was 127.57 m^2/g while that reported in Vassileva *et al.*, 1996 was 84 m^2/g.

b: Studied at pH 8 and the adsorption capacity was originally reported in unit of µg/g .

c: Studied at pH 8 and the adsorption capacity was originally reported in unit of mmol/g.

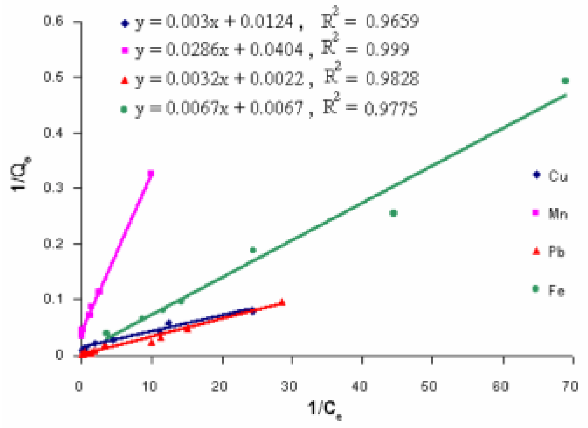

Figure 6. Langmuir isotherm plots for Mn(II), Fe(III), Cu(II), and Pb(II). (The data points are mean of three replicates.)

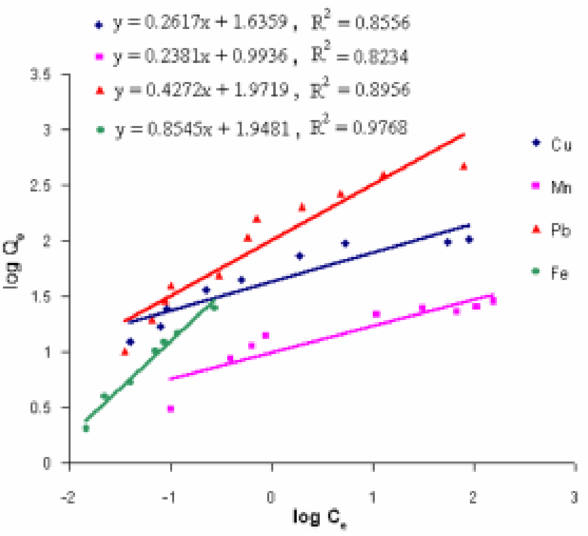

Figure 7. Freundlich isotherm plots for Mn(II), Fe(III), Cu(II), and Pb(II). (The data points are mean of three replicates.)

measured in this work. While the capacity of ha-TiO_2 and the other four comparative TiO_2's for Fe(III) appeared, surprisingly, to be similar at about 15 mg/g even though we expected (1) the ha-TiO_2 should have performed better, and (2) the values of the other four TiO_2's should be different. Be that as it may, this is because of the premature precipitation of $Fe(OH)_3$ when Fe(III) solution was used at higher concentration, hence the concentration of Fe(III) solution was limited to the value given in the Experimental Section. All the data obtained to be about 15 mg/g seem to indicate that the adsorption had not yet reached the upper limit of the capacity each TiO_2 sample could have adsorbed when the premature precipitation took place.

Scheme of the adsorption

Surfaces of metal oxides usually show positive charge at low pH and negative charge at high pH with the PZC and IEP in between (Figure 8). For TiO_2 there have been many reports on PZC and IEP (Table 3) and all are below pH 7.

In this work all the isotherm studies were carried out at pH 7 where the surface of TiO_2 would be slightly negative or readily be changing to negative. The adsorption of the cations (Mn(II), Fe(III), Cu(II), and Pb(II)) on this surface can be

Table 3. Literature values for the point of zero charge (PZC) and iso-electric points (IEP) of TiO_2.

Type of TiO_2	PZC	IEP	Refs.
Anatase (Tioxide Ltd.)	6.2	-	Malati and Smith, 1979
Anatase	-	6.2	Vassileva *et al.*, 1996
Anatase (Sachtleben)	-	5.6	Winkler and Marme, 2000
Rutile (Tioxide Ltd.)	5.3	-	Malati and Smith, 1979
Nanocrystalline microporous	5.7	-	Poznyak *et al.*, 1999
Hydrous TiO_2	5.0	5.0	Ottaviani *et al.*, 1985

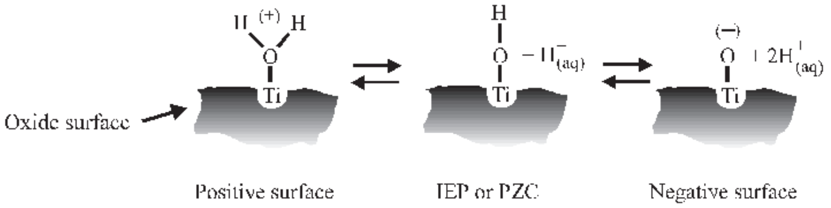

Figure 8. Nature of surfaces at metal oxide-water interfaces, adapted from Schindler, 1981.

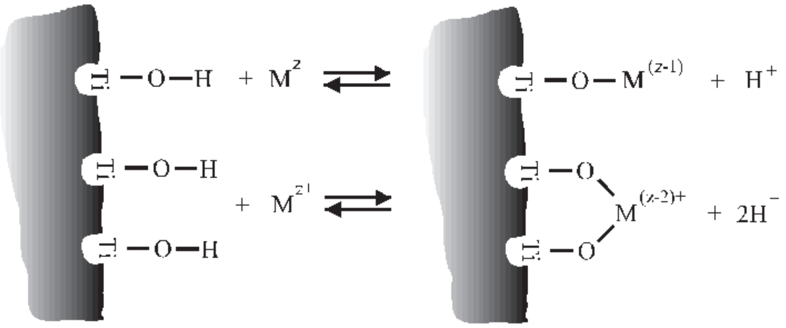

Figure 9. Deprotonated surface hydroxyls yielded negatively-charged surface and readily adsorbed cations, adapted from Schindler, 1981. (M = Mn(II), Fe(III), Cu(II), Pb(II)).

illustrated in Figure 9 as shown by Schindler, 1981.

Conclusion

Titanium dioxide synthesized in this work, ha-TiO_2, exists as hydrated amorphous form with high surface area. This ha-TiO_2 can adsorb metal ions, Mn(II), Fe(III), Cu(II) and Pb(II), better than TiO_2 in any other crystalline forms. The adsorption of Mn(II) , Cu(II) , and Pb(II) on ha-TiO_2 surface clearly conforms to the Langmuir isotherm while the Fe(III) case is somewhat ambiguous since it conforms equally well to both the Langmuir and Freundlich isotherms.

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